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Addition of tetrachloromethane to alkenes catalyzed by copper(I) complexes with *N*-thioacylamidothiophosphate ligands

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Abstract

The catalytic activity of copper(I) complexes with *N*-thioacylamidothiophosphate ligands towards addition reaction of tetrachloromethane to alkenes was investigated. The influence of nucleophilic co-catalysts (alcohols, *N*-heterocycles, etc.) on catalytic activity of metal complexes was determined.

Keywords: Kharasch reaction; Homogeneous catalysis; Copper(I) complexes

1. Introduction

The addition of polyhalogenated alkanes to carbon–carbon double bonds (Kharasch reaction [1]) is one method of forming C–C bonds and it has been applied to the synthesis of polyfunctional acyclic and heterocyclic compounds (β-aminoacids [2], alkaloids [3] and others).

This reaction has been of interest during the last 50–60 years. Primarily organic peroxides were used as initiators for this process. However, in the presence of free-radical initiators not only adduct 1:1, but also different telomerhomologues are obtained [4]. Exploration of the catalytic activity of metal complexes in the Kharasch process has increased the sphere of synthetic application of this reaction. In the presence of metal complexes, it is possible for the reaction to proceed in mild conditions, and to significantly increase the selectivity of the process.

Intense interest in copper complexes applied in the Kharasch reaction and related processes is connected with its attractive activity/cost ratio [5,6]. The analysis of literature data shows that a restricted range of copper catalysts was investigated previously in this process, and in most cases an excess of polyhalogenated alkane (i.e. five-fold) was needed to achieve a good yield of the target product.

This work is devoted to the investigation of the catalytic activity of copper(I) complexes with *N*-thioacylamidothiophosphate ligands [7–9] applied to the addition reaction of CCl_4 to alkenes.

2. Results and discussion

2.1. Addition of tetrachloromethane to 1-hexene in the presence of mononuclear copper(I) complexes

The addition of tetrachloromethane to 1-hexene was taken as a model (Scheme 1). We have found that copper(I) complexes with *N*-thioacylamidothiophosphate ligands can catalyze the process to give 1,1,1,3-tetrachloroheptane as a main product. Catalytic activity of the complexes is represented in Table 1 (the conversion of 1-hexene was less than 1% when the initial rate was determined; the rate of the non-catalyzed reaction $(1.8 \pm 0.13) \times 10^{-8}\,\mathrm{mol\,l^{-1}\,s^{-1}}$ is three orders of magnitude lower than in the presence of catalyst, so the influence of non-catalyzed reactions for the further kinetic measurement was neglected). As follows from Table 1, the composition and structure of the ligand has a major influence on the catalytic activity. Previously [10] it was suggested that there is no correlation between donating ability of phosphine ligands ($P(p\text{-}CF_3C_6H_4)_3$,

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